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(54) NEW PRODUCTION OF SPINEL TYPE LITHIUM MANGANESE COMPOUND OXIDE  
AND POSITIVE ELECTRODE ACTIVE SUBSTANCE FOR SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a compound oxide having improved discharge cycle characteristics under a high-temperature environment by suspending a conjugated manganese hydroxide compound in a water medium, adding an aqueous solution containing borate ion and a specific amount of a water-soluble lithium compound to the suspension, spray or freeze drying and baking at a prescribed temperature.

SOLUTION: A compound of formula II ( $Mp^{+}$  is a p-valent ((p)=2-3) metal cation selected from  $Al^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ,

$Li^{+}$ ,  $Mn^{2+}$ ,  $Mg^{2+}$ ,  $B^{3+}$ ,  $Co^{2+}$

$Mn^{2+}$ ,  $Co^{2+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Al^{3+}$ ,  $Li^{+}$ ,  $B^{3+}$ ,  $Mg^{2+}$

I

II

$\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ca}^{3+}$  and  $\text{Mg}^{2+}$ ;  $\text{An}^-$  is an n-valent ((n) is 1-2) anion such as  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{CH}_3\text{COO}^-$  or the like;  $0 \leq a \leq 0.25$ ;  $0.03 < z < 0.3$ ;  $0 < m$ ) is used to give a spinel type compound oxide of formula I (M is Al, Cr, Fe, Ni, Co, Ga or Mg;  $0.9 \leq x \leq 1.1$ ;  $y = y_1 + y_2$ ;  $0.002 \leq y \leq 0.5$ ;  $0 \leq y_1 < 0.5$ ;  $0.002 \leq y_2 \leq 0.1$ ). A conjugated manganese hydroxide compound and a water-soluble lithium compound are added in the molar ratio of  $\text{Li}/(\text{Mn}+\text{B})$  or  $\text{Li}/(\text{Mn}+\text{M}+\text{B})$  of 0.45-0.55 and a slurry is spray or freeze dried and baked at 600-900°C.

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## CLAIMS

## [Claim(s)]

## [Claim 1] A general formula (I)

$\text{Li}_x\text{Mn}_{(2-y)}\text{My}_1\text{B}_y\text{O}_4$  (I) (M is at least one kind of metal chosen from a group which consists of aluminum, Cr, Fe, nickel, Co, Ga, and Mg among a formula) In a manufacture method of a spinel mold lithium manganese multiple oxide which x is  $0.9 \leq x \leq 1.1$ , and y is  $y = y_1 + y_2$ , and is shown by  $0.002 \leq y \leq 0.5$ ,  $0 \leq y_1 \leq 0.5$ , and  $0.002 \leq y_2 \leq 0.1$  A general formula (II) (II) (among a formula)  $\text{Mn}^{2+}_{(1-a)}\text{M}^{p+}_a(\text{OH})_{[2-(2-p)-a-nz]}(\text{An}^-)_z \cdot m\text{H}_2\text{O}$   $\text{M}^{p+}$  is at least one kind of p \*\* chosen from a group which consists of aluminum<sup>3+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, nickel<sup>2+</sup>, Co<sup>2+</sup>, Ga<sup>3+</sup>, and Mg<sup>2+</sup>. (p=2-3) A metal cation, An- An anion of n \*\* (n=1-2), such as NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, and CH<sub>3</sub>COO<sup>-</sup>, A compound manganese hydroxide compound shown is made to suspend under water data medium. a, z, and m -- respectively --  $0 \leq a \leq 0.25$ ,  $0.03 < z < 0.3$ , and  $0 < m$  -- being shown -- Add an aqueous solution containing boric-acid ion, and express a water-soluble lithium compound with a mole ratio to all metals in water data medium. It adds in a range used as 0.45-0.55 [however, in the case of a= 0, it restricts in a general formula (II)], or mole-ratio =0.45-0.55 of Li/(Mn+M+B). mole-ratio [ of Li/(Mn+B) ] = -- A manufacture method of a spinel mold lithium manganese multiple oxide characterized for an obtained slurry by fuel spray or freeze-drying and calcinating at 600-900 degrees C.

[Claim 2] General formula (Ia)  $\text{Li}_x\text{Mn}_{(2-y)}\text{MyO}_4$  (Ia) (M is at least one kind of metal chosen from a group which consists of aluminum, Cr, Fe, nickel, Co, Ga, and Mg among a formula) In a manufacture method of a spinel mold lithium manganese multiple oxide shown x --  $0.9 \leq x \leq 1.1$  -- it is -- y --  $0.002 \leq y \leq 0.5$  -- being shown -- A general formula (IIa) (IIa) (among a formula)  $\text{Mn}^{2+}_{(1-a)}\text{M}^{p+}_a(\text{OH})_{[2-(2-p)-a-nz]}(\text{An}^-)_z \cdot m\text{H}_2\text{O}$   $\text{M}^{p+}$  is at least one kind of p \*\* chosen from a group which consists of aluminum<sup>3+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, nickel<sup>2+</sup>, Co<sup>2+</sup>, Ga<sup>3+</sup>, and Mg<sup>2+</sup>. (p=2-3) A metal cation, An- An anion of n \*\* (n=1-2), such as NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, and CH<sub>3</sub>COO<sup>-</sup>, a, z, and m -- respectively --  $0.001 \leq a \leq 0.25$ ,  $0.03 < z < 0.3$ , and  $0 < m$  -- being shown -- a compound manganese hydroxide compound shown and a water-soluble lithium compound in water data medium A mole ratio of Li/(Mn+M) = a manufacture method of a spinel mold lithium manganese multiple oxide which adds in a range used as 0.45-0.55, and is characterized for an obtained slurry by fuel spray or freeze-drying and calcinating at 600-900 degrees C.

[Claim 3] A general formula (II) or (IIa) a compound manganese hydroxide compound of a display by general formula (II) a case of a! =0, or in the case of a general formula (IIa) A mixed aqueous solution of a water-soluble salt of a metal expressed that M/(Mn+M) atomic ratio is set to 0.001-0.25 by a water-soluble salt of Mn and M is prepared under water data medium. A simultaneous adding reaction is performed so that this mixed aqueous solution and an alkali aqueous solution may be set to eight or more pH. It is obtained by method of filtering an acquired resultant and rinsing, or by general formula (II) in the case of a= 0 A manufacture method of a spinel mold lithium manganese multiple oxide according to claim 1 or 2 which

prepares a water-soluble salt water solution of Mn, and is obtained by method of filtering a resultant acquired by performing a simultaneous adding reaction, and rinsing so that this aqueous solution and an alkali aqueous solution may be set to eight or more pH.

[Claim 4] A general formula (II) or (IIa) a compound manganese hydroxide compound of a display by general formula (II) a case of  $a \neq 0$ , or in the case of a general formula (IIa) A mixed aqueous solution of a water-soluble salt of a metal expressed to a water-soluble salt of Mn and M that  $M/(Mn+M)$  atomic ratio is set to 0.001-0.25 4 is prepared under water data medium. Under stirring, add an alkali aqueous solution in this mixed aqueous solution, and it is obtained by method of making pH of a system maintaining and reacting or more to eight, or by general formula (II) in the case of  $a = 0$  A manufacture method of a spinel mold lithium manganese multiple oxide according to claim 1 or 2 obtained under stirring in a water-soluble salt water solution of Mn by method of adding an alkali aqueous solution, and keeping pH of a system or more at eight, and making it react.

[Claim 5] A manufacture method of a spinel mold lithium manganese multiple oxide according to claim 3 or 4 characterized by performing a generation reaction of a general formula (II) or (IIa) a compound manganese hydroxide compound of a display under a non-oxidizing atmosphere.

[Claim 6] A manufacture method of a spinel mold lithium manganese multiple oxide according to claim 3 or 4 characterized by performing a generation reaction of a general formula (II) or (IIa) a compound manganese hydroxide compound of a display under existence of a reducing agent and a non-oxidizing atmosphere.

[Claim 7] By general formula (II), a case of  $a \neq 0$  or (IIa) manufacture of a compound manganese hydroxide compound of a display A metaled mixed aqueous solution and a metaled alkali aqueous solution of a water-soluble salt which are expressed by a water-soluble salt of Mn and M are continuously supplied to a reaction vessel with overflow with each metering pump. A manufacture method of a spinel mold lithium manganese multiple oxide according to claim 3 which is made to react to the bottom of churning by eight or more pH, leads an overflowing resultant slurry to a thickener, and is characterized by being carried out by method of returning to a reaction vessel continuously by using as a seed a slurry condensed with a thickener.

[Claim 8] Positive active material for rechargeable lithium-ion batteries characterized by containing a spinel mold lithium manganese multiple oxide manufactured by method according to claim 1 or 2 as an active principle.

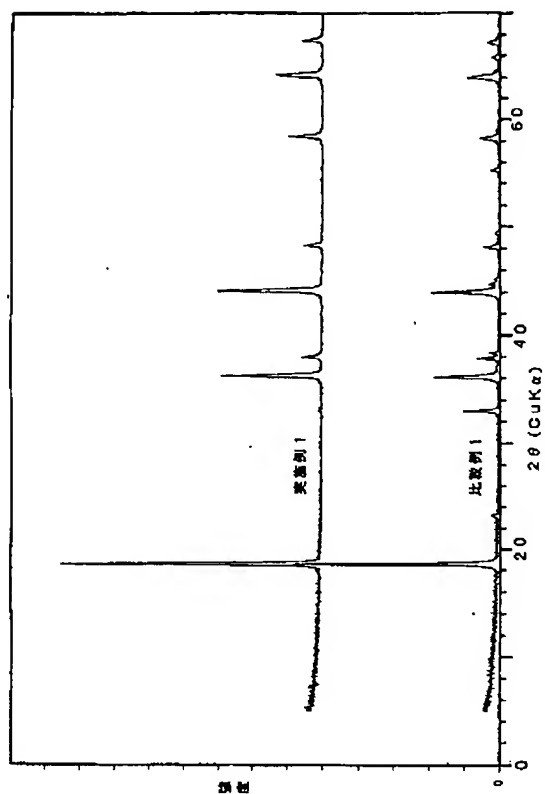
[Claim 9] Positive active material for rechargeable lithium-ion batteries according to claim 8 with which a charge-and-discharge property under an elevated temperature has been improved.

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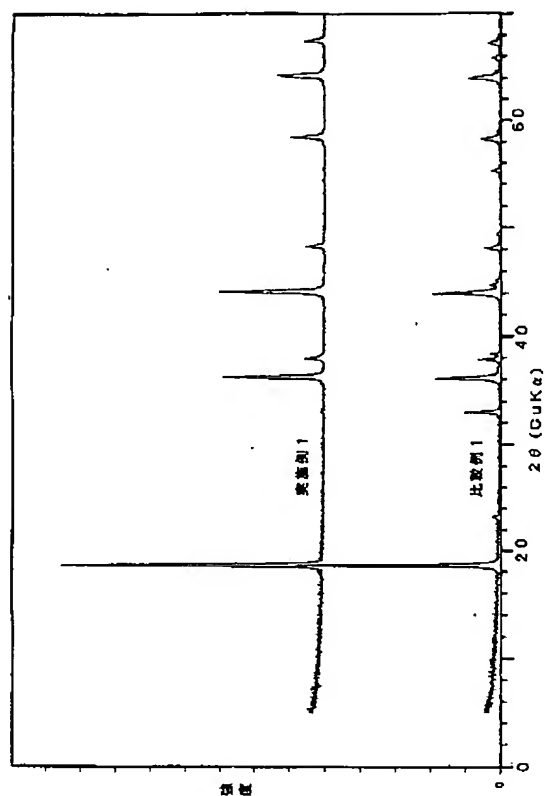


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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the positive active material for rechargeable lithium-ion batteries which consists of a spinel mold lithium manganese multiple oxide manufactured by the manufacture method of the spinel mold lithium manganese multiple oxide with which the charge-and-discharge cycle property under an elevated temperature (50 degrees C or more) has been improved, and this method.

[0002]

[Description of the Prior Art] In recent years, with the miniaturization of small electronic equipment, and carrying-izing, it is lightweight and the need of the lithium secondary battery which has high energy density is increasing. The spinel mold  $\text{LiMn}_2\text{O}_4$  which can serve as a positive-electrode material of 4V system lithium ion battery also in it is abundant in the manganese which is a raw material in resource, and moreover, since it is cheap, it is observed as a cell material for general-purpose articles, such as an electric vehicle.

[0003] However, although the spinel mold  $\text{LiMn}_2\text{O}_4$  is a material in which a comparatively high cell capacity is shown, there is a problem in the elution to the cycle property in charge and discharge especially the cycle property under an elevated temperature (50 degrees C or more), or the electrolytic solution of Mn etc.

[0004] In order to solve such a trouble, replacing a part of Mn in spinel mold  $\text{LiMn}_2\text{O}_4$  structure with other metals is proposed. This is  $\text{MnO}_6$  octahedron which has arranged oxygen in the six directions, Since the ionic radius of Mn located at the center of structure is large, the crevice between the oxygen atoms located in the outside of octahedron increases, and it becomes instability structurally, but by replacing the ion located at the center of octahedron with ion smaller than Mn, since packing becomes [ the crevice between oxygen atoms ] few well, structure is stable. Furthermore, the reactivity over the electrolytic solution falls and it is expected that Mn elution to the electrolytic solution will decrease notably.

[0005] As the manufacture method of a multiple oxide that other metals replaced a part of Mn Although the methods (JP,4-289662,A, JP,2-220358,A, etc.) replaced with aluminum, the method (JP,8-195200,A) replaced by B, or the method (JP,9-245836,A) replaced by Cr and Fe is indicated Since it is the so-called dry process calcinated after any manufacture method carries out powder mixing of the oxide of Mn insoluble in water or a hydroxide, and other metal components, that to which the metal which it was going to replace dissolved to homogeneity at Mn is not obtained. Therefore, what the elution to the charge-and-discharge cycle property which is the defect of  $\text{LiMn}_2\text{O}_4$  especially the cycle property under an elevated temperature (50 degrees C or more), or the electrolytic solution of Mn fully solved is not yet obtained.

[0006] Moreover, although Mn system rechargeable battery attracts attention as power supply materials, such as notebook sized personal computers, such as an electric vehicle, these things are used under comparatively hot environment rather than ordinary temperature in



many cases, and an improvement of the charge-and-discharge cycle property in an elevated temperature is desired.

[0007]

[Problem(s) to be Solved by the Invention] This invention makes a part of Mn dissolve to homogeneity with other metals, and aims at offering the positive active material for rechargeable lithium-ion batteries which consists of a spinel mold lithium manganese multiple oxide manufactured by the manufacture method of the spinel mold lithium manganese multiple oxide with which the charge-and-discharge cycle property under elevated-temperature (50 degrees C or more) environment has been improved, and this method.

[0008]

[Means for Solving the Problem] this invention persons are general formulas (I) obtained by process of this invention, as a result of inquiring wholeheartedly, in order to solve the above-mentioned technical problem.

$\text{Li}_x\text{Mn}_{(2-y)}\text{M}_y\text{O}_4$  (I) (M is at least one kind chosen from a group of aluminum, Cr, Fe, nickel, Co, Ga, and Mg among a formula) It is the general formula (Ia) whose  $y_2$  is 0 in the above-mentioned general formula (I) and  $x$  is  $0.9 \leq x \leq 1.1$ ,  $y$  is  $y = y_1 + y_2$  and  $0.002 \leq y \leq 0.5$ ,  $0 \leq y_1 < 0.5$ , and  $0.002 \leq y_2 \leq 0.1$  are shown.

$\text{Li}_x\text{Mn}_{(2-y)}\text{M}_y\text{O}_4$  It found out that a spinel mold lithium manganese multiple oxide shown by (Ia) and (M and  $x$  showing the above and this meaning among a formula, and  $y$  showing  $0.002 \leq y \leq 0.5$ ) could solve the above-mentioned technical problem. At least one kind of metal chosen from a group which furthermore consists of aluminum, Cr, Fe, nickel, Co, Ga, Mg, and B replaces a part of Mn, by using what carried out homogeneity dissolution as positive active material for rechargeable lithium-ion batteries, it finds out that a charge-and-discharge property under comparatively hot (50 degrees C or more) environment is improved from ordinary temperature, and this invention is based on these knowledge.

[0009] This invention Namely, (general formula I)  $\text{Li}_x\text{Mn}_{(2-y)}\text{M}_y\text{O}_4$  (I) (M is at least one kind chosen from a group which consists of aluminum, Cr, Fe, nickel, Co, Ga, and Mg among a formula) In a manufacture method of a spinel mold lithium manganese multiple oxide shown  $x - 0.9 \leq x \leq 1.1$  -- it is --  $y - y = y_1 + y_2$  -- it is --  $0.002 \leq y \leq 0.5$  and  $0 \leq y - 1 < 0.5$  and  $0.002 \leq y_2 \leq 0.1$  -- being shown -- General formula (II) (II) (among a formula)  $\text{Mn}_{2+(1-a)}\text{M}_p + a(\text{OH})_{[2-(2-p) - a - n_z]} (\text{An}^-)_z$  and  $m\text{H}_2\text{O}$   $\text{M}_p$  is at least one kind of  $p^{**}$  chosen from a group which consists of  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ga}^{3+}$ , and  $\text{Mg}^{2+}$ . ( $p=2-3$ ) Metal cation,  $\text{An}^-$  An anion of  $n^{**}$  ( $n=1-2$ ), such as  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{CH}_3\text{COO}^-$ , A compound manganese hydroxide compound shown is made to suspend under water data medium.  $a$ ,  $z$ , and  $m$  -- respectively --  $0 \leq a \leq 0.25$ ,  $0.03 < z < 0.3$ , and  $0 < m$  -- being shown -- Add an aqueous solution containing boric-acid ion, and express a water-soluble lithium compound with a mole ratio to all metals in water data medium. It adds in a range used as  $0.45-0.55$  [however, in the case of  $a=0$ , it restricts in a general formula (II)], or mole-ratio  $=0.45-0.55$  of  $\text{Li}/(\text{Mn}+\text{M}+\text{B})$ . mole-ratio [ of  $\text{Li}/(\text{Mn}+\text{B})$  ] = -- A manufacture method of a spinel mold lithium manganese multiple oxide characterized for an obtained slurry by fuel spray or freeze-drying and calcinating at 600-900 degrees C, and a general formula whose  $y_2$  is 0 in the above-mentioned general formula (I) (Ia)

$\text{Li}_x\text{Mn}_{(2-y)}\text{M}_y\text{O}_4$  In a manufacture method of a spinel mold lithium manganese multiple oxide shown by (Ia) and (M and  $x$  showing the above and this meaning among a formula, and  $y$  showing  $0.002 \leq y \leq 0.5$ ) General formula (IIa) (IIa) (among a formula)  $\text{Mn}_{2+(1-a)}\text{M}_p + a(\text{OH})_{[2-(2-p) - a - n_z]} (\text{An}^-)_z - m\text{H}_2\text{O}$  A metal cation of at least one kind of  $p^{**}$  ( $p=2-3$ ) chosen from a group which  $\text{M}_p$  becomes from  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ga}^{3+}$ , and  $\text{Mg}^{2+}$ ,  $\text{An}^-$  An anion of  $n^{**}$  ( $n=1-2$ ), such as  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{CH}_3\text{COO}^-$ ,  $a$ ,  $z$ , and  $m$  -- respectively --  $0.001 \leq a \leq 0.25$ ,  $0.03 < z < 0.3$ , and  $0 < m$  -- being shown -- a compound manganese hydroxide compound shown and a water-soluble lithium compound in water data

medium A mole ratio of  $\text{Li}/(\text{Mn}+\text{M}) =$  it is the manufacture method of a spinel mold lithium manganese multiple oxide which adds in a range used as 0.45-0.55, and is characterized for an obtained slurry by fuel spray or freeze-drying and calcinating at 600-900 degrees C.

[0010] A manufacture method of this invention has two features so that it may state below. A metal expressed with a case of  $y_1 \neq 0$  or a general formula (Ia) by manganese hydroxide by Above M, i.e., at least one kind of metal chosen from aluminum, Cr, Fe, nickel, Co, Ga, and Mg, has the first feature in a compound manganese hydroxide compound (II) dissolved or combined or (IIa) compounding by general formula (I). By compounding such a compound manganese hydroxide compound, where at least one kind of metal cation expressed to Mn before baking by Above M is dissolved or combined with homogeneity, it can calcinate. Moreover, it is in compounding a manganese hydroxide salt shown at  $\text{Mn}^{2+}(\text{OH}) [2-\text{nz}] (\text{An}-\text{z}-\text{mH}_2\text{O})$  of the general formula (II) display compounds by general formula (I) in the case of  $y_1=0$ .

[0011] In a general formula (I), it can consider as a slurry containing B by making filtration, rinsing, and water suspend a compound manganese hydroxide compound obtained by the above-mentioned composition, and adding an aqueous solution containing boric-acid ion. By this process, B can be added to homogeneity even at a primary particle of the above-mentioned compound manganese hydroxide compound. Furthermore, a spinel mold lithium manganese multiple oxide which is easily shown by general formula (I) and which carried out homogeneity dissolution can be obtained by adding a water-soluble lithium compound in water data medium to the above-mentioned slurry containing B, and drying and calcinating to it.

[0012] In a general formula (Ia), a spinel mold lithium manganese multiple oxide which is easily shown by general formula (Ia) and which carried out homogeneity dissolution can be obtained by making filtration, rinsing, and water suspend a compound manganese hydroxide compound obtained by this composition, adding a water-soluble lithium compound in water data medium, and drying and calcinating.

[0013] Many above-mentioned problems were able to come to solve a multiple oxide of this invention for the first time by improving remarkably a cycle property which is the defect of  $\text{LiMn}_2\text{O}_4$ , especially a charge-and-discharge property comparatively in an elevated temperature (specifically 50 degrees C or more) beyond a room temperature, etc., and using a multiple oxide of this invention as positive active material for rechargeable lithium-ion batteries.

[0014] the second feature – the above-mentioned compound manganese hydroxide compound (II) – or (IIa) it is drying a slurry obtained from a water-soluble lithium compound by spray drying or freeze drying. In order to spray a slurry with a nozzle or a disk atomiser and to dry in an instant, it can dry, while a compound manganese hydroxide compound (II) or (IIa) boric-acid ion, and a water-soluble lithium compound had distributed to homogeneity on primary particle level, and constituent of spray drying is uniform. Moreover, a precursor of a very good general formula (I) and (Ia) can be obtained with heat energy which starts at the time of desiccation. therefore, a spinel system made into the object by calcinating this – it is obtained without the uniform solid solution carrying out the byproduction of the impurity of  $\text{Mn}_2\text{O}_3$  grade, and the homogeneity solid solution which has improved a cycle property, especially a charge-and-discharge property in an elevated temperature is obtained like the first feature. freeze drying – the compound manganese hydroxide solid solution (II) – with or (IIa), since it can dry in the condition that the homogeneity of a constituent which a water-soluble lithium compound distributed to homogeneity on primary particle level is high, a precursor of a multiple oxide shown by very good general formula (I) and (Ia) can be obtained.

[0015] A spray drying method that fuel spray or a freeze drying method can be mentioned, and it can dry as the desiccation method of the above-mentioned slurry in an instant, and a spherical object can be obtained to a large quantity is more desirable from a homogeneous viewpoint of spherical granulation nature and a constituent.

[0016] Since bulk density of a dry matter is raised by request, it can also calcinate, after casting by methods, such as compression molding. In order to perform compression molding of a dry matter, a spray drying article is desirable from an especially industrial field.

[0017] In addition, about an ambient atmosphere to desiccation, although there is especially no limit, it may be performed by request under a non-oxygen ambient atmosphere, for example, nitrogen-gas-atmosphere kind. Generation of  $Mn^{3+}$  can be controlled and the oxide solid solution made into the object is easy to be obtained by carrying out under a non-oxygen ambient atmosphere. Moreover, generation of  $Mn^{3+}$  can be controlled like a non-oxygen ambient atmosphere, and the oxide solid solution made into the object is easy to be obtained by carrying out by making organic system reducing agents, such as inorganic system reducing agents, such as a reducing agent, for example, a lithium borohydride, a boron hydride potassium, and a sodium borohydride, and an ascorbic acid, exist at the time of composition. Although especially an addition of a reducing agent is not restricted, what is necessary is just usually 1 - 10 % of the weight per reaction capacity.

[0018] What contains an anion which vaporizes at the time of baking as a water-soluble lithium compound is used suitably. Since a lithium hydroxide, a lithium nitrate, oxalic acid lithiums, or these hydrates are anions which volatilize at the time of baking as a water-soluble lithium compound, for example, it is suitable. In this invention, one or more kinds can be chosen and used for arbitration out of these compounds.

[0019] A boric acid can be mentioned as B. A boric acid can be easily dissolved in water.

[0020] The above-mentioned general formula (II) and a manganese hydroxide compound of a display (IIa) which are used for manufacture of a spinel mold multiple oxide shown by general formula (I) of this invention and (Ia) can be obtained by the following manufacture methods.

[0021] In the case of  $a \neq 0$ , in a list by general formula (II) namely, in the case of a general formula (IIa) By hydrogamy general formula (II), a case of  $a \neq 0$ , or in the case of a general formula (IIa) A mixed aqueous solution of a water-soluble salt of a metal expressed that  $M/(Mn+M)$  atomic ratio is set to 0.001-0.25 by a water-soluble salt of Mn and M is prepared under water data medium. It is obtained by method of filtering a resultant acquired by performing a simultaneous adding reaction, and rinsing so that this mixed aqueous solution and an alkali aqueous solution may be set to eight or more pH. Or by general formula (II), a water-soluble salt water solution of Mn is prepared, under stirring in this aqueous solution, in the case of  $a = 0$ , it reacts by adding alkali and keeping pH of a system or more at eight, and it is acquired by filtering and rinsing an acquired resultant. Remaining as it is or water is made to suspend this thing, and it can be used for degree process. While the above-mentioned reaction carries out bubbling of the nitrogen under a non-oxygen ambient atmosphere, it carries out under strong churning, and especially case of reaction temperature where it considers as 25 degrees C, and residence-time 30 minutes is desirable.

[0022] As alkali used by this invention, it is the hydroxide of alkaline metals etc., for example, a sodium hydroxide, a potassium hydroxide, a lithium hydroxide, etc. can be mentioned. It is a sodium hydroxide preferably.

[0023] A general formula (II) or (IIa) inner An- can show an anion of  $n^{**}$ , for example, can mention anions, such as  $NO_3^-$ ,  $Cl^-$ ,  $Br^-$ ,  $CH_3COO^-$ ,  $CO_3^{2-}$ , and  $SO_4^{2-}$ . They are  $NO_3^-$  and  $CO_3^{2-}$  preferably.

[0024] If various metallic compounds shown by M used for manufacture of this invention are water-soluble things, there will be especially no limit. For example, a metal carbonate, a metal nitrate, a thing that carries out the organometallic complex origin can be mentioned. It is shown below preferably. As a water-soluble salt of manganese, for example, as a water-soluble salt of aluminum, a manganese sulfate, manganese nitrate, a manganese chloride, etc. As a water-soluble salt of Cr, an aluminum chloride etc. Chromium-nitrate 9 hydrate etc., As a water-soluble salt of Fe, ferric chloride and iron nitrate 9 hydrate etc. can mention a

magnesium chloride etc. as a nitric-acid gallium and a water-soluble salt of Mg as water-soluble salts of Ga, such as cobalt nitrate 6 hydrate, as nickel nitrate and a water-soluble salt of Co as a water-soluble salt of nickel.

[0025] It can manufacture also by so-called seed circular-reaction method stated to a manganese hydroxide compound (II) used as a start raw material in this invention, or (IIa) the following. namely, a water-soluble salt of Mn and M (it Co(es) aluminum, Cr, Fe, and nickel --) An aqueous solution containing a water-soluble salt expressed by at least one kind in Ga and Mg, or a water-soluble salt and an alkali aqueous solution of Mn each constant rate For example, it is the manufacture method which supplies a reaction vessel with overflow continuously using a pump, is made to react to the bottom of churning by eight or more pH, leads an overflowing resultant slurry to a thickener, and is continuously returned to a reaction vessel by using as a seed a slurry condensed with a thickener. According to this process, bulk density can manufacture easily the solid solution of about two or more manganese hydroxide compounds.

[0026] Although baking can be performed in atmospheric air and under a hyperoxia ambient atmosphere, it is under desirable more economical atmospheric air.

[0027] 600-900 degrees C of 700-800 degrees C of burning temperature are 750 degrees C more preferably. What has cell capacity sufficient below 600 degrees C is not obtained, but it becomes easy to decompose a product at temperature exceeding 900 degrees C. It is not necessary to control especially a firing environments, and the bottom of atmospheric air is enough for it.

[0028] Firing time is about 10 hours more preferably for 5 to 20 hours for 1 hour or more, although there is especially no limit. In order to raise bulk density after baking by request, it can also calcinate, after casting by methods, such as compression molding.

[0029] Thus, (general formula I) (Ia)  $\text{Li}_x\text{Mn}_{(2-y)}\text{My}_1\text{By}_2\text{O}_4$  of obtained this invention (I)  $\text{Li}_x\text{Mn}_{(2-y)}\text{MyO}_4$  A spinel mold lithium manganese multiple oxide shown by (Ia) can be effectively used as positive active material for rechargeable lithium-ion batteries.

[0030] A cell trial of positive active material of this invention examined by a method shown in an example of a trial mentioned later following, and creating a cel for a trial. An improvement of a charge-and-discharge property under elevated-temperature (50 degrees C or more) environment put a created cel for a trial into a 60-degree C thermostat, and checked by performing charge and discharge.

[0031] As a negative electrode of a rechargeable lithium-ion battery which used a spinel mold lithium manganese multiple oxide of this invention for positive active material, a compound which can occlusion emit a lithium metal, a lithium alloy, or a lithium can be used. As a lithium alloy, a lithium / tin alloy, a lithium/aluminum alloy, a lithium/lead alloy, etc. are mentioned, for example. Moreover, carbonaceous materials, such as a graphite and graphite, etc. can be mentioned as a compound in which lithium occlusion bleedoff is possible.

[0032] Although especially the electrolytic solution is not restricted, at least one kind of organic solvent of ether, such as lactone, such as sulfolanes, such as carbonate, such as propylene carbonate and diethyl carbonate, a sulfolane, and dimethyl sulfoxide, and gamma-butyrolactone, and dimethoxyethane, can be used, for example.

[0033] Although especially an electrolyte is not restricted, what dissolved at least one kind of lithium salt, such as lithium perchlorate, a 4 boron-fluoride lithium, a 6 fluoride [ phosphoric-acid ] lithium, and a trifluoro methansulfonic acid lithium, into the above-mentioned solvent, a solid electrolyte of lithium ion conductivity of an inorganic system and an organic system, etc. can be used, for example.

[0034]

[Example] Hereafter, an example explains this invention more concretely.

[0035] 100ml of mixed aqueous solutions of the manganese nitrate of 2.0mol/l and an

aluminium nitrate was prepared so that the atomic ratio of example 1aluminum/(Mn+aluminum) might be set to 0.05, and this mixed aqueous solution was added in 100ml of sodium-hydroxide aqueous solutions of 4.0mol/l. In addition, the reaction was performed under strong churning also as that of nitrogen bubbling, and reaction temperature was made into 25 degrees C. The slurry of 1mol/l expressed with empirical formula  $\text{Mn}_{0.941}\text{aluminum}_{0.051}(\text{OH})_{1.988}(\text{NO}_3)_{0.047} \cdot 0.10\text{H}_2\text{O}$  was obtained by making water suspend the obtained reaction mixture after filtration and rinsing under nitrogen-gas-atmosphere mind. (In addition, this empirical formula dries some resultants at ejection and 110 degrees C overnight, and is the same also in other examples) . Spray drying was performed, after the atomic ratio trickled the 3.0 mol/l lithium-hydroxide aqueous solution of the amount equivalent to  $\text{Li}/(\text{Mn}+\text{aluminum}) = 0.51$  and made it react to (Mn+aluminum) of this suspension. Actuation from washing to desiccation was performed in the environment where a non-oxidizing atmosphere (nitrogen-gas-atmosphere mind) is maintained. The obtained desiccation gel was put into the boat made from an alumina, and the fine particles which calcinate 750 degrees C for 10 hours, crack with an agate mortar, and are expressed with a tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) with empirical formula  $\text{Li}_{0.997}\text{Mn}_{1.907}\text{aluminum}_{0.093}\text{O}_4$  under atmospheric air were obtained.

[0036] All the peaks of the X-ray of X-ray diffraction drawing of the obtained fine particles were what belongs to the spinel mold  $\text{LiMn}_2\text{O}_4$ .

[0037] The lattice constant was 8.16Å.

[0038] Addition of the ascorbic acid was carried out 2% (w/v) to a mixed aqueous solution capacity at the mixed aqueous solution of the manganese sulfate of 2.0mol/l, and an aluminum sulfate so that example 2aluminum / (Mn+aluminum) atomic ratio might be set to 0.05, and it and the sodium-carbonate aqueous solution of 2.5mol/l were prepared.

Simultaneous adding was performed so that it might become a reaction pH 9.0 about the two above-mentioned sorts of solutions, and the sodium-hydroxide aqueous solution of 4.0mol/l, and the successive reaction was performed in reaction temperature [ of 25 degrees C ], and residence-time 30 minutes. The so-called seed circular reaction which puts the obtained liquid into a thickener continuously and is returned to a reaction layer at speed 20 times the speed of raw material addition after concentration was performed. The slurry of 1mol/l expressed with empirical formula  $\text{Mn}_{0.920}\text{aluminum}_{0.080}(\text{OH})_{2.000}(\text{CO}_3)_{0.040} \cdot 0.11\text{H}_2\text{O}$  was obtained by making water suspend the obtained reaction mixture after filtration and rinsing. Spray drying was performed, after the atomic ratio trickled 3.0 mols / 1 lithium-hydroxide aqueous solution of the amount equivalent to 1.0mol/l- $\text{H}_3\text{BO}_3$  equivalent to  $\text{B}/(\text{Mn}+\text{aluminum}) = 0.02$ , and  $\text{Li}/(\text{Mn}+\text{aluminum}+\text{B}) = 0.51$  and made it react to (Mn+aluminum) of this suspension. The obtained desiccation gel was put into the boat made from an alumina, and the fine particles which calcinate 750 degrees C for 10 hours, crack with an agate mortar, and are expressed with a tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) under atmospheric air with empirical formula  $\text{Li}_{1.010}\text{Mn}_{1.800}\text{aluminum}_{0.016}\text{B}_{0.040}\text{O}_4$  were obtained.

[0039] All the peaks of the X-ray of X-ray diffraction drawing of the obtained fine particles were what belongs to the spinel mold  $\text{LiMn}_2\text{O}_4$ .

[0040] The lattice constant was 8.15Å.

[0041] It carried out similarly except not using aluminum of example 3 example 2. That is, addition of the ascorbic acid was carried out 2% (w/v) to aqueous solution capacity at the manganese-sulfate aqueous solution of 2.0mol/l, and it and the sodium-carbonate aqueous solution of 2.5mol/l were prepared. Simultaneous adding was performed so that it might become a reaction pH 9.0 about the two above-mentioned sorts of solutions, and the sodium-hydroxide aqueous solution of 4.0mol/l, and the successive reaction was performed in reaction temperature [ of 25 degrees C ], and residence-time 30 minutes. The so-called seed

circular reaction which puts the obtained liquid into a thickener continuously and is returned to a reaction layer at speed 20 times the speed of raw material addition after concentration was performed. The slurry of 1mol/l expressed with empirical formula  $\text{Mn}_{1.000}(\text{OH})_{1.954}(\text{CO}_3)_{0.023} \cdot 0.09\text{H}_2\text{O}$  was obtained by making water suspend the obtained reaction mixture after filtration and rinsing. Spray drying was performed, after the atomic ratio trickled 3.0 mols / 1 lithium-hydroxide aqueous solution of the amount equivalent to 1.0mol/l- $\text{H}_3\text{BO}_3$  equivalent to  $\text{B}/\text{Mn}=0.02$ , and  $\text{Li}/(\text{Mn}+\text{B})=0.51$  and made it react to Mn of this suspension. The obtained desiccation gel was put into the boat made from an alumina, and the fine particles which calcinate 750 degrees C for 10 hours, crack with an agate mortar, and are expressed with a tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) under atmospheric air from empirical formula empirical formula  $\text{Li}_{1.013}\text{Mn}_{1.960}\text{B}_{0.040}\text{O}_4$  were obtained.

[0042] All the peaks of the X-ray of X-ray solution diffraction drawing of the obtained fine particles were what belongs to the spinel mold  $\text{LiMn}_2\text{O}_4$ .

[0043] The lattice constant was 8.17Å.

[0044] Weighing capacity of lithium-hydroxide monohydrate, a manganese dioxide, and the aluminium nitrate (all use a special grade chemical and the Wako Pure Chem make) was carried out, after mixing and desiccation gel were fully put into the board made from an alumina with the agate mortar, and 900 degrees C was calcinated under atmospheric air with the tubular furnace for 10 hours so that it might become example of comparison 1aluminum / (Mn+aluminum) atomic ratio 0.05, and the  $\text{Li}/(\text{Mn}+\text{aluminum})$  atomic ratio 0.51. The fine particles which crack a baking object with an agate mortar and are expressed with empirical formula  $\text{Li}_{1.004}\text{Mn}_{1.903}\text{aluminum}_{0.097}\text{O}_4$  were obtained.

[0045] That by which the peak of the X-ray of X-ray diffraction drawing of the obtained fine particles belongs to  $\text{Mn}_2\text{O}_3$  other than the spinel mold  $\text{LiMn}_2\text{O}_4$  was observed.

[0046] The lattice constant was 8.20Å.

[0047] Weighing capacity of lithium-hydroxide monohydrate, a manganese dioxide, and the oxidation (all use a special grade chemical and the Wako Pure Chem make) was carried out, after mixing and desiccation gel were fully put into the board made from an alumina with the agate mortar, and 900 degrees C was calcinated under atmospheric air with the tubular furnace for 10 hours so that it might become example 2B of a comparison / (Mn+B) atomic ratio 0.04, and the  $\text{Li}/(\text{Mn}+\text{B})$  atomic ratio 0.51. The fine particles which crack a baking object with an agate mortar and are expressed with empirical formula  $\text{Li}_{1.013}\text{Mn}_{1.960}\text{B}_{0.040}\text{O}_4$  were obtained.

[0048] That by which the peak of the X-ray of X-ray diffraction drawing of the obtained fine particles belongs to  $\text{Li}_2\text{B}_4\text{O}_7$  other than the spinel mold  $\text{LiMn}_2\text{O}_4$  was observed.

[0049] The lattice constant was 8.20Å.

[0050] The following cell tests (charge-and-discharge test) were performed using each multiple oxide of the example of trial 1 above-mentioned example 1, and the example 1 of a comparison.

[0051] Into the positive-electrode material, 16mg was mixed for TAB-2 as  $\text{Li}_x\text{Mn}_{(2-y)}\text{MyO}_4$  25mg obtained in the above-mentioned example and the example of a comparison, and a conductive binder, compression molding was performed on a stainless steel mesh, and the pellet with a diameter of 18mm was obtained. The obtained pellet was dried at 200 degrees C for 2 hours or more, and it considered as the positive-electrode material.

[0052] The porous membrane made from polypropylene (Celgard 2502) and a glass filter filter paper were used for the diaphragm using what stuck the rolling lithium metal sheet by pressure on the stainless steel base at the negative-electrode material.

[0053] From the assembly of the cel for a trial (half-release mold cel) to finishing was performed all over the dry box which carried out argon substitute using the ethylene



carbonate/dimethyl carbonate (1:2) which dissolved one mol / 1 LiPF<sub>6</sub> in the electrolytic solution. Charge and discharge were performed for this cel for a trial between 3.5-4.5V by the constant current density of 0.4 mA/cm<sup>2</sup>. Initial discharge capacity (mAh/g), the 50th discharge capacity (mAh) /g, and the 50th attenuation factor (%) were as being shown in a table 1 as a result of this cell trial.

[0054]

[A table 1]

試料番号	初期 放電容量 (mAh/g)	50回目 放電容量 (mAh/g)	50回目 減衰率 (%)
実施例 1	112.8	111.2	1.4
	114.5	113.6	0.6
	113.5	112.4	1.0
比較例 1	90.6	63.8	29.8
	74.5	68.2	8.5
	83.7	72.5	13.4

[0055] The manganese nitrate solution of example of comparison 31.0 mol/l was prepared, simultaneous adding was performed so that this aqueous solution and the sodium-hydroxide solution of 1.0 mol/l might be set to pH9.0, and the successive reaction was performed. In addition, the reaction was performed under strong churning also as that of nitrogen bubbling, and reaction temperature was made into 25 degrees C, and residence-time 30 minutes. The slurry of 1 mol/l expressed with empirical formula Mn<sub>1.000</sub>(OH)<sub>1.949</sub>(NO<sub>3</sub>)<sub>0.051</sub>·0.10H<sub>2</sub>O was obtained by making water suspend the obtained reaction mixture after filtration and rinsing. Spray drying was performed, after the atomic ratio trickled the 3.0 mol/l lithium-hydroxide aqueous solution of the amount equivalent to Li/Mn=0.51 and made it react to Mn of this suspension. The obtained desiccation gel was put into the boat made from an alumina, and the fine particles which calcinate 750 degrees C for 10 hours, crack with an agate mortar, and are expressed with a tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) from empirical formula Li<sub>1.062</sub>Mn<sub>1.954</sub>O<sub>4</sub> under atmospheric air were obtained.

[0056] X diffraction drawing of these fine particles is shown in drawing 2. All the peaks of the obtained X-ray were what belongs to the spinel mold LiMn<sub>2</sub>O<sub>4</sub>.

[0057] The lattice constant was 8.23A.

[0058] The mixed aqueous solution of the manganese nitrate of 1.0 mol/l and an aluminium nitrate was prepared so that it might become example 4aluminum / (Mn+aluminum) atomic ratio 0.05. Simultaneous adding was performed so that this mixed aqueous solution and the sodium-hydroxide solution of 1.0 mol/l might be set to pH11.0, and the successive reaction was performed. In addition, the reaction was performed under strong churning also as that of nitrogen bubbling, and reaction temperature was made into 25 degrees C, and residence-time 30 minutes. The slurry of 1 mol/l expressed with empirical formula Mn<sub>0.951</sub>aluminum<sub>0.049</sub>(OH)<sub>1.998</sub>(NO<sub>3</sub>)<sub>0.051</sub>·0.12H<sub>2</sub>O was obtained by making water suspend the obtained reaction mixture after filtration and rinsing. Spray drying was performed, after the atomic ratio trickled the 3.0 mol/l lithium-hydroxide aqueous solution of the amount equivalent to Li/(Mn+aluminum)=0.51 and made it react to (Mn+aluminum) of this suspension. The obtained desiccation gel was put into the boat made from an alumina, and the fine particles which calcinate 750 degrees C for 10 hours, crack with an agate mortar, and are expressed with a tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) with empirical formula Li<sub>0.997</sub>Mn<sub>1.907</sub>aluminum<sub>0.099</sub>O<sub>4</sub> under atmospheric air were obtained.

[0059] X diffraction drawing of these fine particles is shown in drawing 2. All the peaks of the obtained X-ray were what belongs to the spinel mold LiMn<sub>2</sub>O<sub>4</sub>.

[0060] The lattice constant was 8.21Å.

[0061] The manganese nitrate of 1.0 mol/l and the mixed solution of an aluminium nitrate were prepared so that it might become example 5aluminum / (Mn+aluminum) atomic ratio 0.05.

Simultaneous adding was performed so that this mixed solution and the sodium-hydroxide solution of 1.0 mol/l might be set to pH11.0, and the successive reaction was performed. In addition, the reaction was performed under strong stirring under nitrogen bubbling, and reaction temperature was made into 25 degrees C, and residence-time 30 minutes. The slurry of 1 mol/l expressed with empirical formula  $\text{Mn}_{0.950}\text{aluminum}_{0.050}(\text{OH})_{1.994}(\text{NO}_3)_{0.056} \cdot 0.10\text{H}_2\text{O}$  was obtained by making water \*\*\*\* the obtained reaction mixture after filtration and rinsing. Spray drying was performed, after the atomic ratio trickled the 3.0 mol/l lithium-hydroxide aqueous solution of 1.0 mol/l- $\text{H}_3\text{BO}_3$  equivalent to  $\text{B}/(\text{Mn}+\text{aluminum}) = 0.02$ , and the amount equivalent to  $\text{Li}/(\text{Mn}+\text{aluminum}+\text{B}) = 0.51$  and made it react to (Mn+aluminum) of this suspension. The fine particles which crack the obtained desiccation gel with an agate mortar, and are expressed with empirical formula  $\text{Li}_{1.013}\text{Mn}_{1.866}\text{aluminum}_{0.100}\text{B}_{0.040}\text{O}_4$  were obtained.

[0062] X diffraction drawing of these fine particles is shown in [drawing 2](#) . All the peaks of the obtained X-ray were what belongs to the spinel mold  $\text{LiMn}_2\text{O}_4$ .

[0063] The lattice constant was 8.21Å.

[0064] The mixed aqueous solution of the manganese nitrate and the chromium nitrate (III) of 1.0 mol/l was prepared so that it might become example 6Cr / (Mn+Cr) atomic ratio 0.03. It processed like the example 4 below and the slurry of 1 mol/l expressed with empirical formula  $\text{Mn}_{0.970}\text{Cr}_{0.030}(\text{OH})_{1.991}(\text{NO}_3)_{0.039} \cdot 0.12\text{H}_2\text{O}$  was obtained. Spray drying was performed, after the atomic ratio trickled the 3.0 mol/l lithium-hydroxide aqueous solution of the amount equivalent to  $\text{Li}/(\text{Mn}+\text{Cr}) = 0.51$  and made it react to (Mn+Cr) of this suspension. 750 degrees C is calcinated under atmospheric air with a tubular furnace by putting the obtained desiccation gel into the boat made from an alumina for 10 hours, and it cracks with an agate mortar, and is an empirical formula. The fine particles expressed with  $\text{Li}_{1.050}\text{Mn}_{1.924}\text{Cr}_{0.060}\text{O}_4$  were obtained.

[0065] X diffraction drawing of these fine particles is shown in [drawing 2](#) . All the peaks of the obtained X-ray were what belongs to the spinel mold  $\text{LiMn}_2\text{O}_4$ .

[0066] The lattice constant was 8.23Å.

[0067] The manganese nitrate of 1.0 mol/l and the mixed aqueous solution of iron nitrate (III) were prepared so that it might become example 7Fe / (Mn+Fe) atomic ratio 0.03. It processed like the example 4 below and the slurry of 1 mol/l expressed with empirical formula  $\text{Mn}_{0.970}\text{Fe}_{0.030}(\text{OH})_{1.995}(\text{NO}_3)_{0.035} \cdot 0.10\text{H}_2\text{O}$  was obtained. Spray drying was performed, after the atomic ratio trickled the 3.0 mol/l lithium-hydroxide aqueous solution of the amount equivalent to  $\text{Li}/(\text{Mn}+\text{Fe}) = 0.51$  and made it react to (Mn+Fe) of this suspension. The obtained desiccation gel was put into the boat made from an alumina, and the fine particles which calcinate 750 degrees C for 10 hours, crack with an agate mortar, and are expressed with a tubular furnace by empirical formula  $\text{Li}_{1.054}\text{Mn}_{1.876}\text{Fe}_{0.059}\text{O}_4$  under atmospheric air were obtained.

[0068] X diffraction drawing of these fine particles is shown in [drawing 2](#) . All the peaks of the obtained X-ray were what belongs to the spinel mold  $\text{LiMn}_2\text{O}_4$ .

[0069] The lattice constant was 8.23Å.

[0070] The manganese nitrate of 1.0 mol/l and the mixed solution of nickel nitrate were prepared so that it might become example 8nickel / (Mn+nickel) atomic ratio 0.03. It processed like the example 4 below and the slurry of 1 mol/l expressed with empirical formula  $\text{Mn}_{0.971}\text{nickel}_{0.029}(\text{OH})_{1.978}(\text{NO}_3)_{0.022} \cdot 0.12\text{H}_2\text{O}$  was obtained. Spray drying was performed, after the atomic ratio trickled the 3.0 mol/l lithium-hydroxide aqueous solution of the amount equivalent to  $\text{Li}/(\text{Mn}+\text{nickel}) = 0.51$  and made it react to (Mn+nickel) of this suspension.



The obtained desiccation gel was put into the boat made from an alumina, and the fine particles which calcinate 750 degrees C for 10 hours, crack with an agate mortar, and are expressed with a tubular furnace with empirical formula  $\text{Li}_{1.033}\text{Mn}_{1.904}\text{Ni}_{0.059}\text{O}_4$  under atmospheric air were obtained.

[0071] X diffraction drawing of these fine particles is shown in [drawing 2](#) . All the peaks of the obtained X-ray were what belongs to the spinel mold  $\text{LiMn}_2\text{O}_4$ .

[0072] The lattice constant was 8.23Å.

[0073] The mixed aqueous solution of the manganese nitrate and the cobalt nitrate of 1.0 mol/l was prepared so that it might become example 9Co / (Mn+Co) atomic ratio 0.03. It processed like the example 4 below and the slurry of 1 mol/l expressed with empirical formula  $\text{Mn}_{0.970}\text{Co}_{0.030}(\text{OH})_{1.967}(\text{NO}_3)_{0.033} \cdot 0.11\text{H}_2\text{O}$  was obtained. Spray drying was performed, after the atomic ratio trickled the 3.0 mol/l lithium-hydroxide aqueous solution of the amount equivalent to  $\text{Li}/(\text{Mn}+\text{Co}) = 0.51$  and made it react to (Mn+Co) of this suspension. The obtained desiccation gel was put into the boat made from an alumina, and the fine particles which calcinate 750 degrees C for 10 hours, crack with an agate mortar, and are expressed with a tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) by empirical formula  $\text{Li}_{1.022}\text{Mn}_{1.911}\text{Co}_{0.060}\text{O}_4$  under atmospheric air were obtained.

[0074] X diffraction drawing of these fine particles is shown in [drawing 3](#) . All the peaks of the obtained X-ray were what belongs to the spinel mold  $\text{LiMn}_2\text{O}_4$ .

[0075] The lattice constant was 8.23Å.

[0076] The mixed aqueous solution of the manganese nitrate of 1.0 mol/l and a nitric-acid gallium was prepared so that it might become example 10Ga / (Mn+Ga) atomic ratio 0.03. It processed like the example 4 hereafter and the slurry of 1 mol/l expressed with empirical formula  $\text{Mn}_{0.969}\text{Ga}_{0.031}(\text{OH})_{1.992}(\text{NO}_3)_{0.039} \cdot 0.10\text{H}_2\text{O}$  was obtained. Spray drying was performed, after the atomic ratio trickled the 3.0 mol/l lithium-hydroxide aqueous solution of the amount equivalent to  $\text{Li}/(\text{Mn}+\text{Ga}) = 0.51$  and made it react to (Mn+Ga) of this suspension. The obtained desiccation gel was put into the boat made from an alumina, and the fine particles which calcinate 750 degrees C for 10 hours, crack with an agate mortar, and are expressed with a tubular furnace by empirical formula  $\text{Li}_{1.051}\text{Mn}_{1.896}\text{Ga}_{0.060}\text{O}_4$  under atmospheric air were obtained.

[0077] X diffraction drawing of these fine particles is shown in [drawing 3](#) . All the peaks of the obtained X-ray were what belongs to the spinel mold  $\text{LiMn}_2\text{O}_4$ .

[0078] The lattice constant was 8.23Å.

[0079] The mixed aqueous solution of the manganese nitrate and the magnesium nitrate of 1.0 mol/l was prepared so that it might become example 11Mg / (Mn+Mg) atomic ratio 0.03. It processed like the example 4 below and the slurry of 1 mol/l expressed with empirical formula  $\text{Mn}_{0.971}\text{Mg}_{0.029}(\text{OH})_{1.971}(\text{NO}_3)_{0.029} \cdot 0.12\text{H}_2\text{O}$  was obtained. Spray drying was performed, after the atomic ratio trickled the 3.0 mol/l lithium-hydroxide aqueous solution of the amount equivalent to  $\text{Li}/(\text{Mn}+\text{Mg}) = 0.51$  and made it react to (Mn+Mg) of this suspension. The obtained desiccation gel was put into the boat made from an alumina, and the fine particles which calcinate 750 degrees C for 10 hours, crack with an agate mortar, and are expressed with a tubular furnace with empirical formula  $\text{Li}_{1.020}\text{Mn}_{1.928}\text{Mg}_{0.059}\text{O}_4$  under atmospheric air were obtained.

[0080] X diffraction drawing of these fine particles is shown in [drawing 3](#) . All the peaks of the obtained X-ray were what belongs to the spinel mold  $\text{LiMn}_2\text{O}_4$ .

[0081] The lattice constant was 8.23Å.

[0082] The manganese sulfate of 2.0 mol/l, the mixed aqueous solution of an aluminum sulfate, and the sodium-carbonate aqueous solution of 2.5 mol/l were prepared so that it might become example 12aluminum / (Mn+aluminum) atomic ratio 0.05. Simultaneous adding was performed so that the two above-mentioned sorts of solutions and the sodium-hydroxide

aqueous solution of 4.0 mol/l might be set to pH9.0, and the successive reaction was performed in reaction temperature [ of 25 degrees C ], and residence-time 30 minutes. The so-called seed circular reaction which puts the obtained liquid into a thickener continuously and is returned to a reaction vessel at speed 20 times the speed of raw material addition after concentration was performed. The slurry of 1 mol/l expressed with empirical formula  $\text{Mn}_{0.949}\text{aluminum}_{0.051}(\text{OH})_{1.967}(\text{CO}_3)_{0.042} \cdot 0.11\text{H}_2\text{O}$  was obtained by making water \*\*\*\* the obtained reaction mixture after filtration and rinsing. Spray drying was performed, after the atomic ratio trickled the 3.0 mol/l lithium-hydroxide aqueous solution of the amount equivalent to  $\text{Li}/(\text{Mn}+\text{aluminum}) = 0.51$  and made it react to  $(\text{Mn}+\text{aluminum})$  of this suspension. The obtained desiccation gel was put into the boat made from an alumina, it calcinated at 750 degrees C under atmospheric air with the tubular furnace for 10 hours, and the fine particles which crack with an agate mortar and are expressed with empirical formula  $\text{Li}_{1.013}\text{Mn}_{1.894}\text{aluminum}_{0.100}\text{O}_4$  were obtained.

[0083] All the peaks of the X-ray of X diffraction drawing of these fine particles were what belongs to spinel mold  $\text{LiMn}_2\text{O}_4$ .

[0084] The lattice constant was 8.22Å.

[0085] Weighing capacity of lithium-hydroxide monohydrate, a manganese dioxide, and the aluminium nitrate was carried out, after mixing and desiccation gel were fully put into the boat made from an alumina with the agate mortar, and it calcinated at 750 degrees C under atmospheric air with the tubular furnace for 10 hours so that it might become example of comparison 4aluminum /  $(\text{Mn}+\text{aluminum})$  atomic ratio 0.05, and the  $\text{Li}/(\text{Mn}+\text{aluminum})$  atomic ratio 0.51. The fine particles which crack a baking object with an agate mortar and are shown with empirical formula  $\text{Li}_{1.004}\text{Mn}_{1.902}\text{aluminum}_{0.097}\text{O}_4$  were obtained. That by which X diffraction drawing of the obtained fine particles belongs to  $\text{Li}_2\text{MnO}_3$  and  $\text{Mn}_2\text{O}_3$  other than the spinel mold  $\text{LiMn}_2\text{O}_4$  was observed.

[0086] The lattice constant was 8.21Å.

[0087] The following cell tests (charge-and-discharge test) were performed using each multiple oxide of the example of trial 2 above-mentioned examples 5-12, and the example 4 of a comparison.

[0088] Creation and the electrolytic solution of the cel for a trial of a cell test were performed like the example 1 of a trial. After putting the cel for a trial into the 60-degree C thermostat and leaving it for 30 minutes in the state of an open circuit, constant current constant-voltage charge and discharge were performed between 3.5-4.5V with the current density of 0.4 mA/cm<sup>2</sup>. Initial discharge capacity (mAh/g), the 50th discharge capacity (mAh/g), and the 50th attenuation factor (%) were as being shown in a table 2 as a result of this cell trial.

[0089]

[A table 2]

試料 番号	初期 放電容量 (mAh/g)	50回目 放電容量 (mAh/g)	50回目 減衰率 (%)	嵩密度 (g/ml)
比較例 3	131.3	95.6	27.19	1.51
実施例 4	106.5	100.9	5.26	1.39
実施例 5	103.6	96.5	6.85	1.37
実施例 6	120.7	111.7	7.45	1.64
実施例 7	100.9	75.3	25.37	1.41
実施例 8	103.9	102.2	1.64	1.55
実施例 9	123.7	99.2	19.81	1.62
実施例 10	122.2	104.1	14.81	1.49
実施例 11	117.5	101.9	13.28	1.43
実施例 12	100.3	93.2	7.08	2.02
比較例 4	98.3	68.5	30.32	1.42

[0090]

[Effect of the Invention] The general formula by which the charge-and-discharge cycle property under elevated-temperature (50 degrees C or more) environment has been improved by this invention (I)

$\text{Li}_x\text{Mn}_{(2-y)}\text{My}_1\text{By}_2\text{O}_4$  (I) (M is at least one kind chosen from the group which consists of aluminum, Cr, Fe, nickel, Co, Ga, and Mg among a formula) It is the general formula (Ia) whose y is  $y=y_1+y_2$  and whose  $y_2$  x is  $0.9 \leq x \leq 1.1$ , and is 0 in  $0.002 \leq y \leq 0.5$ ,  $0 \leq y_1 < 0.5$ ,  $0.002 \leq y_2 \leq 0.1$ , and the above-mentioned general formula (I).

$\text{Li}_x\text{Mn}_{(2-y)}\text{MyO}_4$  (Ia)

The positive active material for rechargeable lithium-ion batteries which consists of a multiple oxide manufactured by the new manufacture method and this method of the spinel mold lithium manganese multiple oxide shown by (M and x show the above and this meaning among a formula, and y shows  $0.002 \leq y \leq 0.5$ ) was able to be offered.

[0091] The cycle property which is not in the former, especially the charge-and-discharge property in the elevated temperature beyond a room temperature (about 50 degrees C or more) are improved, and the multiple oxide of this invention is very useful on industry.

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[Translation done.]